Electrochimica Acta 173 (2015) 131–138

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Electrospun porous vanadium pentoxide nanotubes as a high-performance cathode material for lithium-ion batteries

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ARTICLE INFO

Article history:
Received 30 March 2015
Received in revised form 6 May 2015
Accepted 11 May 2015
Available online 12 May 2015

Keywords:
vanadium pentoxide
electrospinning
lithium ion batteries
nanotubes

ABSTRACT

In this work, porous vanadium pentoxide (V_2O_5) nanotubes have been synthesized by a simple electrospinning technique followed by an annealing process with using low-cost inorganic vanadium precursor. By controlling the annealing time at 400 °C, a small amount of polymer pyrolysis carbon can be retained which improves the conductivity of the porous V_2O_5 nanotubes. When evaluated as a cathode material for lithium ion batteries, the porous V_2O_5 nanotubes delivered capacities of 114.9, 99.7 and 79.6 mAh g^{-1} at 10, 20 and 50C in the voltage range of 2.5-4.0 V, respectively. Moreover, the porous V_2O_5 nanotubes display good cycling performance, the capacity retention is 97.4% after 200 cycles at 50C. The results indicate that fabricating nanostructured V_2O_5 with a porous interconnected morphology is an effective way to improve the electrochemical performance of V_2O_5.

1. Introduction

Over the past two decades, lithium ion batteries (LIBs) are widely used as the power sources for portable electronics due to their high energy density, long cycle life and excellent safety [1,2]. However, with the growing demands for high-energy and high-power applications such as electrical vehicles (EVs) and hybrid electrical vehicles (HEVs), the energy and power density of the electrode materials need to be further improved [3,4]. The cathode performance has a great influence on the battery performance. Hence, exploration of alternative cathode materials for high-energy and high-power lithium-ion batteries is essential.

Among the current cathode materials, V_2O_5, as a typical intercalation compound with a layered structure, has a large theoretical capacity of 294 mAh g^{-1} when storing two lithium ions, which is higher than those of $LiFePO_4$ (170 mAh g^{-1}) and $LiMn_2O_4$ (148 mAh g^{-1}) [5]. In addition, V_2O_5 has advantages of low cost, abundance and better safety, which make it a promising cathode candidate. However, the practical application of V_2O_5 has been seriously hindered by the slow lithium-ion diffusion, low electronic conductivity, which leads to poor cycling stability and poor rate capability [6–8]. To improve electrochemical performance of the V_2O_5 electrode, fabricating nanostructured V_2O_5 materials such as nanofibers [9], nanowires [10] and nanospheres [11–13] has become one of the most effective methods to enhance the electrochemical performance due to the improved lithium-ion diffusion and electronic conductivity. Among these nanostructures, one-dimensional nanostructures attract much attention due to the following advantages. Firstly, the one-dimensional nanostructures have large aspect ratio which could prevent self-aggregation of nanomaterials effectively. In addition, the one-dimensional nanostructures provide an effective electron transport pathway along the one-dimensional direction. These advantages are beneficial to improve electrochemical performance of the electrode. Dewangan et al. synthesized V_2O_5 nanofiber-bundles by a hydrothermal method using a vanadium hydroxylamido complex as a vanadium precursor [14]. O'Dwyer et al. synthesized VO_x nanotubes through a surfactant-assisted templating method [15]. These prepared cathode materials both have a significant enhancement in electrochemical performance. Besides, the introduction of carbon in metal oxide electrode materials could effectively improve the conductivity, which is another strategy to improve the electrochemical performance [16,17]. Nevertheless, these synthesis processes are complex and time-consuming. Compared to these methods, electrospinning is a simple and versatile process for the fabrication of one-dimensional nanostructures. For example, Cheah et al. synthesized one-dimensional V_2O_5 nanofibers by electrospinning the vanadium precursor containing vanadyl acetylacetonate and polyvinylpyrrolidone [18]. Wang et al. synthesized the V_2O_5 nanotubes and V_2O_5 nanofibers by electrospinning using vanadium (IV) acetylacetone as a vanadium precursor [19]. These materials both exhibited

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http://dx.doi.org/10.1016/j.electacta.2015.05.057
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excellent electrochemical performance. However, at present, most preparations of these V_2O_5 nanomaterials use organic vanadium precusors which are expensive, toxic and easily hydrolyzed. Hence, low-cost and simple synthesis of one-dimensional vanadium pentoxide materials with high performance is still a great challenge.

In this work, we choose commercial V_2O_5 power and oxalic acid as raw materials to get low-cost inorganic vanadium oxalate solution as electrospinning vanadium precursor, and take a facile electrospinning approach followed by annealing to fabricate porous V_2O_5 nanotubes. Moreover, by controlling the annealing time at 400 °C, the retention of a small amount of carbon improves the conductivity of the V_2O_5 nanotubes. When used as the cathode materials for lithium ion batteries, the porous V_2O_5 nanotubes with carbon exhibit high reversible capacity, superior cycling stability and excellent rate capability.

2. Experimental Section

2.1. Materials and synthesis

In a typical synthesis, commercial V_2O_5 powder (5.93 mmol) and $H_2C_2O_4 \cdot 2H_2O$ (17.79 mmol) were dissolved in deionized water (24 mL) under vigorous stirring at 80 °C for about 40 min to form a clear blue vanadium oxalate solution (0.495 M). PVP-DMF solution was formed by dissolving polyvinylpyrrolidone (PVP, Mw=1 300000, 18 g) in DMF (82 g) under vigorous stirring. Then, 4 mL (0.495 M) VOC_2O_4 solution was added into 4 mL 18 wt.% PVP-DMF solution under magnetic stirring to form a homogeneous viscous blue solution. Next, the viscous blue solution was loaded into a plastic syringe with a stainless steel nozzle. The solution was electrospun at a DC voltage of 12 kV and a flow rate of 0.08 mm min^{-1}, with a distance of 14 cm between the nozzle and co0llector. Finally, the as-spun fibers were annealed in a furnace in air at 400 °C, with a heating rate of 0.5 °C min^{-1}.

2.2. Characterization

Thermogravimetric analysis (TGA) was carried out on a thermal analyzer (STA449C) in air with a heating rate of 10 °C min^{-1}. X-ray diffraction (XRD) measurements were performed using a Bruker D8 Focus powder diffractometer (Cu Kα, operation voltage: 40 kV, current: 40 mA). X-ray photoelectron spectroscopy (XPS) analysis was carried out with a Kratos Axis Ultra DLD using the mono Al Kα radiation. Elemental analysis was performed using element analyzer (Vario EL III). The structure and morphology were characterized by scanning electron microscopy (SEM, Nano430) and high resolution transmission electron microscope (HRTEM, JEM-2010HR).

2.3. Electrochemical measurements

The electrochemical performances were investigated using coin-cells (CR2025). The working electrodes were prepared by mixing the active materials (70 wt.%), acetylene black (20 wt.%) and polyvinylidene fluoride (PVDF, 10 wt.%) in N-methyl-2-pyrrolidone (NMP) coated on a aluminum foil. The weights of active materials in the electrodes are from 1.5 mg to 2.0 mg. The lithium foil was used as the counter electrode, and the celgard 2400 membrane was used as the separator. The electrolyte was composed of 1 mol L^{-1} $LiPF_6$ dissolved in a mixture of ethylene carbonate (EC) and diethylcarbonate (DEC) (1:1 by volume). The cells were galvanostatically discharged and charged with a multi-channel battery test system (Neware BTS-640) in the voltage ranges of 2.0–4.0 V and 2.5–4.0 V, respectively. Cyclic voltammograms (CV) measurements were performed on an electrochemical workstation at the scan rate of 0.2 mV s^{-1} over the potential range of 2.0-4.0 V and 2.5-4.0 V. Electrochemical impedance spectroscopy (EIS) was measured by the electrochemical workstation (Zahner IM6ex) in the frequency range from 10 mHz to 100 kHz and the voltage amplitude was 5 mV.

3. Results and Discussion

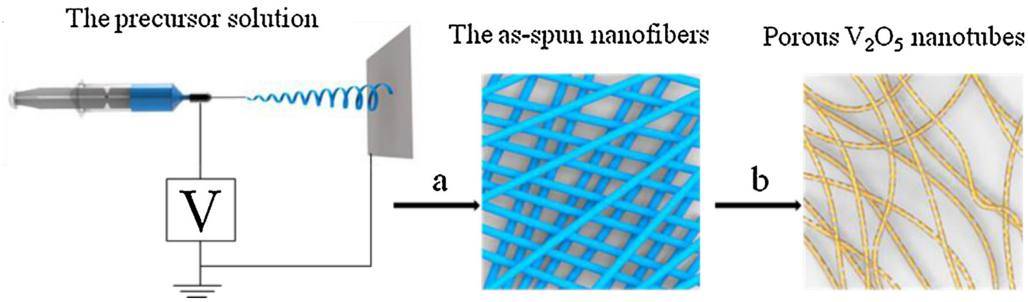
3.1. Microstructure characterization

The water-soluble vanadium oxalate (VOC_2O_4) was prepared according to the following equation: $V_2O_5+3H_2C_2O_4 \rightarrow 2VOC_2O_4+2CO_2+3H_2O$. The electrospinning precursor was prepared by mixing the VOC_2O_4 and PVP-DMF solution. The schematic illustration of the synthesis of the porous V_2O_5 nanotubes is shown in Scheme 1. Firstly, the light blue nanofibers were obtained by electrospinning. Then, the as-spun nanofibers were annealed at 400 °C for 15 min or 60 min, the obtained yellow products were denoted as V_2O_5-15 and V_2O_5-60, respectively.

TGA was performed to investigate thermal decomposition of the as-spun nanofibers. As shown in Fig. 1, the weight loss below the temperature of 200 °C is attributed to the evaporation of moisture and residual solvent (DMF). The thermal decomposition of VOC_2O_4 and degradation of PVP mainly occurs at around 250 °C leading to a weight loss based on a broad exothermic peak near 250 °C in the DSC curve [20]. At about 400 °C, where has an exothermic peak, there is a little weight loss. This may attribute to the oxidation of carbon and release of carbon dioxide [21].

The phases of the calcinated products obtained at 400 °C for 15 min and 60 min were characterized by XRD and the results were shown in Fig. 2. All of the diffraction peaks are indexed to the pure orthogonal symmetry of V_2O_5 (JCPDS card no. 41-1426), which means that the V_2O_5 were both obtained at 400 °C for 15 min and 60 min. There are no obvious peaks of the impurity phase for those two samples.

X-ray photoelectron spectroscopy (XPS) technique was employed to identify the element component (Fig. 3). Fig. 3a shows survey-scan XPS for V_2O_5-15, the peaks corresponding to oxygen, vanadium, and carbon elements. The O(1s) spectrum (Fig. 3b) is broad and asymmetric and could be deconvoluted into



Scheme 1. Electrospinning preparation of porous V_2O_5 nanotubes: (a) electrospinning process; (b) annealing process.